

High-Pressure Transformation Toughening: A Case Study on Zirconia

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Transformation-toughened zirconia compacts have been produced using a pressure-induced phase of zirconia as the toughening agent. The high-pressure phase is retained metastably after compaction at 8.6 GPa and sintering at temperatures as low as 250°C. High-pressure processing offers potential for new transformation-toughening phases in other ceramic materials.

TRANSFORMATION toughening is now well-known as a process by which a material becomes more resistant to crack propagation.¹ In the special case of zirconia, the "classical" transformation-toughened ceramic, the necessary dense metastable transformation-toughening phase is obtainable via a conventional thermal route, by either using a fine particle powder or incorporating an appropriate stabilizing additive.² The production of high-density phases at elevated temperatures, however, is the exception rather than the rule; only a few materials are known to exhibit such anomalous behavior. On the other hand, transformations induced by high pressure invariably involve an increase in density, thus greatly expanding

the number of potential metastable transformation-toughening phases.

EXPERIMENTAL PROCEDURE AND RESULTS

Previous work has shown that the high-pressure phase of pure zirconia can be partially retained at 100 kPa (1 atm) after a

pressure cycle.³ Accordingly, we have carried out some preliminary experiments on zirconia compacts prepared at various temperatures and pressures in a diamond anvil cell.⁴ Fine-grain powders (grain size 0.02 to 0.03 μm) provided the starting material, in nominally pure and doped (12 wt% yttria) forms.* The reason for including the doped material was that it showed no high-pressure transformation,⁴ so that it could be used as a control to distinguish between pressure-sintering and phase-transformation effects.

The various pressure-temperature-time conditions investigated are summarized in Table I. All powders were first preheated to 400°C to remove volatile contaminants. After cooling, these powders were placed in an Inconel[†] gasket within the diamond anvil cell. Those specimens which were to be subjected to temperature sintering (see below) were given another

*ZYP-type powders, Zircor Products, Inc., Florida, NY.

[†]Huntington Alloy Products Div., International Nickel Co., Inc., Huntington, WV.

Table I. Sintering Conditions, Phase Content, and Mechanical Properties of Zirconia Pressure Compacts

Pressure (GPa)	Temperature (°C)	Time (h)	High-pressure phase (%)	Hardness (GPa)	Toughness (MPa·m ^{1/2})
ZrO ₂					
3.5	20	0.5	0	*	*
7.6	20	0.5	0	*	*
3.2	150	0.5	0	*	*
5.0	250	0.5	0	4.4	*
8.6	250	1.5	40	10.3	>4.5
8.5	500	1.5	50	13.0	>4.5
8.5	500	4.0	60	12.0–16.9	≈4.4
ZrO ₂ ·12 wt% Y ₂ O ₃					
8.6	250	1.5		8.9	0.6
8.5	500	4.0		≈10	*

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*Member, the American Ceramic Society.

*Ill-defined crack pattern; very low toughness.

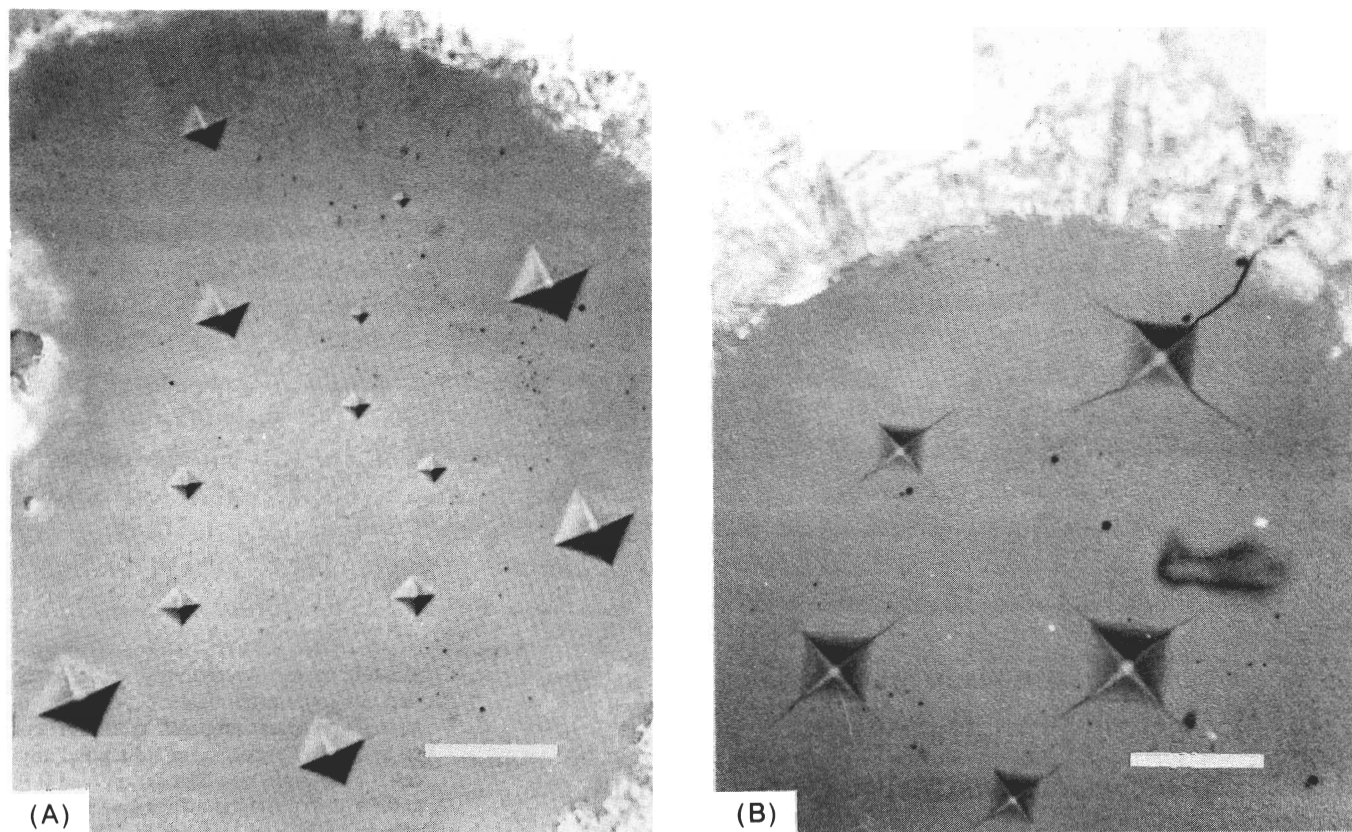


Fig. 1. Micrographs comparing indentation patterns in (A) pure and (B) yttria-doped (12 wt%) zirconia after pressure sintering (bars=50 μm).

preheat treatment, to 250°C for 15 min, to remove any newly absorbed contaminants. Pressure was then applied and, where specified in Table I, the temperature was raised to sinter the compact. Time of sintering was measured from the instant the appropriate pressure-temperature condition was attained. Pressure was released at the sintering temperature except for specimens sintered at 500°C; in this last case the temperature was first reduced to 250°C.

The compacts thus prepared were analyzed for phase composition by energy-dispersive X-ray powder diffraction. The pure zirconia starting material was monoclinic at room temperature and pressure; the doped material was cubic. Only the monoclinic pure material showed a high-pressure phase transformation which required ≈ 8 GPa to drive the transformation in the powder to completion. This high-pressure phase could be metastably retained at ambient pressure and temperature in some of the compacts, depending on the experimental procedure followed. From the X-ray data, the relative amounts of the metastable phase retained in the compacts could be estimated to within $\approx \pm 10\%$. This information is included in Table I.

Microindentation tests were then used to measure the hardness and toughness of the compacts.⁵ Figure 1 illustrates the indentation patterns for pure and doped materials prepared under identical conditions, 8.6 GPa and 250°C for 1.5 h. Although of

only slightly greater hardness (Table I), the pure material is much tougher than its doped counterpart, as evidenced by the distinct lack of radial cracking at the impression corners. This superior toughness is attributable to the presence of the high-pressure metastable phase. We see this correlation between fracture resistance and phase content clearly in the remaining data listed in Table I. The pure specimens compacted at less than 8 GPa produced low-hardness indentations with ill-defined crack patterns; these specimens tended to disintegrate easily, indicating virtually no toughness. The doped specimens fared little better, although pressures of >8 GPa were applied. For those pure specimens prepared at 8.5 GPa and 500°C for 4 h (the most severe treatment), approximately half the indentations showed some signs of cracking, albeit very faint. Although approximate, the estimate of 4.4 $\text{MPa}\cdot\text{m}^{1/2}$ for the toughness shows that the region of behavior of conventional transformation-toughened zirconias is being approached.

DISCUSSION

Our preliminary results, therefore, demonstrate the potential for using high pressure as a route to transformation toughening. We have been able to achieve a new toughening phase in zirconia compacts at temperatures well below those required to produce the analogous (but structurally different) toughening phase in pressureless

heat treatments. The compacts containing this high-pressure phase show superior mechanical properties. The thermodynamic requirements for retention of this phase at ambient conditions have been examined in some depth, and will be described elsewhere.⁶ Thus, the present study opens up the prospect of using high-pressure methodology as an investigative tool in the search for new transformation-toughening agents in ceramics. Such investigations are currently under way, not only to identify these new agents but also to reduce the pressure levels necessary to form them and to expand the temperature ranges over which they remain in the requisite metastable state.

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